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Abstract

Natural and alkaline modified pumice stones were used for the adsorption of water hardening cations, Ca^{+2} and Mg^{+2}. The adsorbents were characterized using XRF, XRD, SEM and FTIR instrumental techniques. At equilibrium time and for 150 mg/L of a given cation, removal efficiencies were 83% and 94% for calcium and 48% and 73% for magnesium for raw and modified pumices, respectively. The optimal pH for raw and modified pumices were found to be 6.0, leading to the removal of 79 and 96% of calcium and 51 and 93% of magnesium by 10 g/L of raw and modified pumice adsorbents, respectively. Maximum adsorption capacities were 57.27 and 62.34 mg/g for Ca^{+2} and 44.53 and 56.11 mg/g for Mg^{+2} on the raw and modified pumices, respectively. Ca^{+2} and Mg^{+2} adsorption capacities of the pumice adsorbents decreased in the presence of competing cations. Less than 300 minutes were needed to achieve 99 and 92% desorption of the adsorbed Ca^{+2} and 100 and 89% of the adsorbed Mg^{+2} from the natural and modified pumices, respectively. After treating synthetic water solution simulating an actual water stream with the alkali-modified pumice, total hardness of the treated sample met the required standard for drinking water, namely below 300 mg/L of $CaCO_3$ (297.5 mg/L). The studied pumice adsorbents, and especially the treated pumice, can be therefore considered as promising low cost adsorbents, suitable for the removal of hardness ions from drinking water.

Keywords: Calcium; Magnesium; Adsorption; Modification; Batch system

1. Introduction

Most of the water resources should be treated for purification before consumption. In some countries, groundwater is the main safe drinking water resource [1]. In some cases, the resource does not satisfy to the desirable levels regarding their chemical properties, such as hardness, nitrate contamination, heavy metals, soluble iron, etc. [2]. Among them, water hardness can appear problematic in some cases; it can also be considered as an important aesthetic parameter. However, because public acceptance of hardness differs remarkably according to local conditions, a maximum acceptable level has not been defined. In general, water supplies with total hardness higher than 200 mg/L can be tolerated by consumers but are considered as poor resources; while values higher than 500 mg/L are not acceptable for most of the domestic consumptions. Hardness in water refers to existing divalent ions, such as iron, manganese, calcium and magnesium. Among them, calcium and magnesium are known as the dominant species for water hardening [3]. Although it has been shown that water hardness doesn't have serious health impact, it has been demonstrated that hard water is responsible for the formation of deposits in boiler and household facilities, as well as diverse influence on cleaning performances of detergents [4]. Formation of precipitates may cause a decrease of heat transfer in boiler, a decrease of fluid rate, bursting of water pipeline, the formation of stain in dishes and clothes. Furthermore, high concentrations of magnesium in drinking water may induce a bitter taste [5]. In water purification and treatment plant, lime and soda ash are used for the removal of hardness. One of the main drawbacks of this process is the resulting waste, namely the large amount of liquid sludge produced, as well as the need for re-carbonation of the softened water [6, 7]. In addition, the use of additional chemicals to prevent sludge production is restricted and hence in most cases water hardness species cannot be fully removed [8]. Ion exchange processes have been considered as an alternative

approach which is commercially in use worldwide. However, high power consumption and periodical regeneration of saturated ion-exchanger resins are needed. Potential hazards of the effluent solutions resulting from the regeneration process should also be taken into account [9].

Recently, various methods including electrodeionization process [7], electromembrane processes [8], capacitive deionization [9], membrane and fluidized pellet reactor [10], ion exchange process [11-13] and adsorption [14, 15] have been studied for the removal of a wide variety of ionic and molecular species from various water streams, including those responsible for hardness (e.g. Ca^{+2} and Mg^{+2} cations). Amongst the developed processes, adsorption has been widely studied for the uptake of various ionic and molecular species form water. Although the efficiency of activated carbon (AC) as an adsorbent, it cost remains its main drawback. Hence, finding inexpensive and efficient adsorbents remains a topical matter to water treatment industries [16]. Pumice stone is a volcanic rock which corresponds to solidified frothy lava formed when highly pressurized and super-heated rock is vigorously erupted from a volcano. Pumice can also be formed from the mixing of hot lava with water. This unnatural formation is considered as a result of simultaneous rapid cooling and depressurization. The depressurization creates bubbles (i.e. pores) by lowering the solubility of water and CO_2 molecules dissolved in the lava, causing a rapid release of gases. The simultaneous cooling and depressurization trap the bubbles inside the pumice matrix; resulting in highly porous pumice with a very low density (0.35-0.65 g/cm^3), a high water absorption capacity (20-30%) and mainly composed of SiO_2 and Al_2O_3. Considering these physicochemical characteristics, it can be considered as a potential adsorbent for environmental applications [17]. Pumice has been tested for the removal of sulfur dioxide [18], chromium [19], phenol and 4-chlorophenol [20]. The main objective of this research was to evaluate a raw pumice stone and its alkali-modified form (i.e. NaOH-

treated) for the removal of calcium and magnesium from a synthetic solution simulating the Karaj Water Supply System (Iran).

2. Materials and Methods

2.1. Chemicals and solutions

All chemicals used in this work were obtained from Merck (Merck Co. Germany). 0.05 M H_2SO_4 and 0.1 M NaOH were used for pH adjustment (Jenway, model 3510). $MgSO_4.7H_2O$ and $CaCl_2$ were used for the preparation of stock solutions using deionized water. The electrical conductivity of the stock solutions was in the range of 21–26 μs/cm (Jenway, model 4520). A solution containing chloride (450 mg/L), nitrate (25 mg/L) and sulfate (325 mg/L) was prepared. Conductivity and total dissolved solid (TDS) of water solutions were adjusted by adding 1150 mg/L sodium chloride leading to a conductivity of 1850 μs/cm, which corresponded to that of the Karaj water supply system. Raw pumice stone was obtained from Tikmeh Dash Reign of East Azerbaijan (Azerbaijan, Iran). All experiments were conducted according to the Standard Methods for the Examination of Water and Wastewater [21].

2.2. Preparation of the Adsorbent

Raw pumice stone was washed several times with distilled water before use in order to remove any impurities until the turbidity value became lower than 0.1 NTU. The adsorbent was then treated with 1 M solution of HCl for further purification by dissolving acid soluble components of the sample. It was then washed with deionized water to remove the excess of acid (pH= 7). Pumice was then dried at 55^{o}C for 24 hours to evaporate the remaining water molecules. The dried pumice was then milled and sieved to achieve 10-30 meshes (2000 to 841 microns). In order to modify the pumice stone with sodium hydroxide, it was treated with 2 M NaOH for 24 hours at room temperature. During modification, the solution was stirred at 200 rpm. The modified pumice was then filtered and calcined at 750°C for 6 h in an electrical

furnace (Lenton, England). The calcined sample was then washed several times with deionized water to remove the excess of NaOH. The modified adsorbent was then dried at 55^{o}C for 24 h before use.

2.3. Batch Experiments

All experiments were conducted in batch mode in 250 mL conical flasks. Several operating parameters including pH (2-10), temperature (10-50^{o}C), adsorbent mass (2-10 g/L), initial calcium and magnesium concentrations (25-150 mg/L) and contact time were investigated. Optimized adsorption times for natural and modified pumice adsorbents were first examined by varying the contact time at room temperature, pH= 6.0 and for an adsorbent mass of 6 g per liter of solution. For this purpose, 6 g of adsorbent were added to 1 L of solution in a conical flask containing Ca^{+2} or Mg^{+2} cations at a concentration in the range of 25 to 150 mg/L. The mixture was then shaken at 200 rpm (Hanna-Hi 190M, Singapore). Samples were taken at predetermined time intervals, filtered (0.45 μ, Wathman), centrifuged (Sigma-301, Germany) and the ion concentration was measured by a titration method [21]. The removal efficiency (RE) was determined as follows (Eq. 1):

$$RE = (C_0 - C_e) \times 100 / C_0 \qquad (1)$$

After investigation of the effect of the contact time and the initial ion concentration, the effects of pH and adsorbent mass were examined. The effect of temperature was then investigated in the optimal conditions for pH, adsorbent mass and contact time, for three initial concentrations of Ca^{+2} or Mg^{+2} cations (50, 100 and 150 mg/L).

2.4. Adsorbent effect on electrical conductivity (EC) and turbidity

In order to measure the influence of adsorbents on EC and turbidity of water, 6 g/L of natural or modified adsorbent was poured into 250 mL of deionized water (i.e. free from calcium and magnesium) at pH=6.0 and shaken for 200 min at 200 rpm. At predetermined

time intervals, samples were taken for conductivity and turbidity measurements (Jenway, Model 4520).

2.5. Isotherm study

Equilibrium experiments were conducted in 250 mL conical flasks by adding 6 g/L of natural or alkali modified pumice stone to 250 mL of magnesium or calcium solutions at concentrations ranging from 25 to 150 mg/L. The mixture was shaken at 200 rpm for 6 hours at 25^{o}C to ensure that maximum sorption was achieved. The adsorption results were then analyzed by Langmuir, Freundlich and Temkin isotherm models.

The Langmuir isotherm model is based on the assumption of a homogenous surface energy distribution. The non-linear (Eq. 2) and linear (Eq. 3) forms of the Langmuir model are described as follows:

$$q_e = {}^{(q_m b C_e)}\!\!\diagup\!\!_{(1+bC_e)} \qquad (2)$$

$$C_e \diagup q_e = C_e \diagup q_m + 1 \diagup (q_m b) \qquad (3)$$

Where q_e is the equilibrium amount of adsorbate (mg/g), C_e the equilibrium concentration of adsorbate (mg/L), q_m the maximum adsorption capacity (mg/g) and b (L/mg) the Langmuir constant. The important feature of the Langmuir model can be described based on the R_L parameter expressed by Eq. (4):

$$R_L = 1 \diagup (1 + bC_0) \qquad (4)$$

Adsorption is unfavorable for $R_L > 1$, linear for $R_L = 1$, favorable for $0 < R_L < 1$ and irreversible for $R_L = 0$.

The Freundlich isotherm model that is appropriate for heterogeneous systems is expressed by equations (5) and (6).

$$q_e = K_f C_e^{1/n} \quad (5)$$

$$\log(q_e) = \log K_f + 1/n \log C_e \quad (6)$$

Where q_e is the amount of adsorbate (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_f ($mg^{1-1/n}L^{1/n}/g$) and $1/n$ are the Freundlich constants. Large values of K_f reveals high affinity of the adsorbate. For a favorable adsorption, the value of the Freundlich constant (n) should be in the range of 1 to 10.

The Temkin isotherm is also available for heterogeneous surface adsorption. The non-linear and linear forms of the Temkin model are given by Eq. (7) and Eq. (8):

$$q_e = (RT/b_1) \ln(k_t C_e) \quad (7)$$

$$q_e = B_1 \ln(k_t) + B_1 \ln(C_e) \quad (8)$$

Where $B_1=RT/b_1$, b_1 is the adsorption heat (kJ/mol) and k_t is the equilibrium binding constant (L/g) corresponding to the maximum binding energy. A high value of b_1 shows a fast sorption of adsorbate at initial stage. Similarly, a low value of k_t is related to weak bonding of adsorbate onto the medium. By plotting q_e vs. ln(C_e) one can deduce b_1 and k_t from the slope and the intercept of this curve, respectively.

2.6. Kinetic modeling

Kinetic sorption of calcium and magnesium onto natural and alkali-modified pumice adsorbents were investigated by adding 6 g/L of natural and modified adsorbent into 250 mL solution containing 50, 100 and 150 mg/L of the considered cation. The pH of the solution was adjusted at 6.0 and shaken at 200 rpm until reaching equilibrium time. The kinetic of sorption was analyzed by means of the pseudo-second order model, which is expressed as follows:

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (9)$$

Where k_2 is the rate constant (g/mg min). Integration of Eq. (9) at the boundary, q_t=0 at t=0 and q_t=q_t at t=t and then rearrangement to a linear form gives (Eq. 10):

$$t/q_t = 1/k_2 q_e^{\,2} + 1/q_e\, t \qquad (10)$$

The value of k_2 and q_e can be determined from the slope and the intercept of the plot t/q_t vs. t, respectively.

2.7. Determination of the zero point charge

The zero point charge was determined using 0.01 M solution of NaCl as an electrolyte and by adding 0.1 M solutions of NaOH or HCl. For this purpose, the pH of eight beakers containing 50 mL of electrolyte was set to the desirable values in the range of 2 to12. Then 0.5 gram of adsorbent was added into each beaker and shaken for 48 hours. After completion of the reaction, the adsorbent was filtered and the final pH of each beaker was measured. By plotting the initial pH versus the pH after 48 hours of agitation, the zero point charges of the adsorbents were determined, which were found to be 6.3 and 6.5 for natural and modified pumices, respectively.

2.8. Binary System Test

Calcium and magnesium co-exist in actual water streams. Series of experiments were conducted to investigate the effects of one another regarding the adsorption behavior. 6 g/L of adsorbent was added to 250 mL solution containing calcium and magnesium (100 mg/L each). The solution was then shaken at 200 rpm at room temperature for 4 hours (as equilibrium time). Samples were taken at predetermined time intervals, filtered and calcium and magnesium concentrations were measured.

2.9. Regeneration of the spent adsorbents

Regeneration tests for saturated natural and modified pumices were carried out by adding 6 g/L of spent adsorbent in 2 M solution of NaOH. For adsorbent saturation, 6 g/L of adsorbent were let in contact with 250 mL solution containing 100 mg/L calcium or magnesium and stirred at 200 rpm until equilibrium time was reached (240 minutes). The spent adsorbent was filtered, washed and dried at 55^{o}C for 24 h. The dried spent adsorbent was let in contact of 2 N NaOH for 500 min; then filtered, washed several times with deionized water and dried at 55^{0}C for 24 h. The regenerated adsorbent was then tested for the adsorption of calcium and magnesium and the regeneration percentage was calculated based on the comparison of the removal efficiencies of fresh and regenerated adsorbents.

3. Results and Discussion

3.1. Adsorbent Characteristics

Natural and modified adsorbents were characterized by means of various instrumental techniques including X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared spectroscopy (FTIR). Chemical composition of the natural pumice, which was conducted by XRF, is shown in Table 1 [17, 19]. The main chemical components of natural pumice were SiO_2 (63.45%) and Al_2O_3 (17.24%) resembling natural zeolite composition [22]. Alkali modification of the natural pumice by means of sodium hydroxide affected the SiO_2 and Al_2O_3 contents, which increased to 66.34% and 23.32% respectively.

The specific surface area of the adsorbents was measured using the BET technique. It showed a significantly higher specific surface area for the modified pumice if compared to the natural one, 36.30 and 2.34 m^2/g respectively. The remarkable improvement of the

surface area can most likely be attributed to the removal of components occupying the pores of the pumice resulting in more accessible pores and consequently larger surface area.

The XRD patterns of the natural and modified pumice adsorbents are illustrated in Fig.1. While the existence of crystalline phases in the natural and modified pumice samples can be ascribed to the peaks at $2\theta=12.0^0$, 26.0^0, 28.0^0, 32.5^0, 33.0^0, 33.5^0, 34.5^0 and 28.0^o; the observed dome between 2θ= 20 to 40 can be considered as an evidence for the presence of some amorphous phase in both samples. However, the decrease of the dome's height (i.e. area of the dome) in the modified sample can be attributed to a decrease of the amorphous phase in the modified pumice.

SEM micrographs showing surface morphology of the natural and modified pumice adsorbents at magnification of 500X are displayed in Fig. 2. While the surface of the natural adsorbent showed irregular texture with larger grains and sharper edges, the alkali treated pumice showed a deeply re-structured texture with finer particles size and smoother surface.

Fig. 3 shows the Fourier transform infrared spectroscopy (FTIR) of the natural (a) and modified (b) pumices at wavelengths in the range 400–4000 cm^{-1}. The absorption band at ~1043 cm^{-1} was the characteristic peak of $(SiO_4)^{2-}$ groups due to the symmetric stretching vibration of Si–O–Si. The peaks at ~784 and ~464cm^{-1} can be assigned to bending vibrations of Si–O–Si bond. The small peak at ~615 cm^{-1} can be assigned to the regional vibration of reductive carbon in crystal lattice. Other peaks can be assigned to adsorbed water molecules including the broadening peak at ~3449 cm^{-1} that belongs to the asymmetric stretching vibration of H-O bond and the peak at ~1640 cm^{-1} can be assigned to the bending vibration of H–O–H bond. Overall, a high similarity appeared between both IR spectra, in agreement with the available literature [23].

3.2. Effect of the electrical conductivity (EC) and the turbidity

Partial dissolution of an adsorbent in the surrounding solution can influence the adsorption process impacting metal uptake capacity. EC and turbidity tests were conducted and showed an increase with time for both natural and modified pumices samples (Fig.4). EC for natural and modified pumices increased from 6 to 20 µs/cm and 11 to 36 µs/cm, respectively. This increase can be attributed to the presence of some soluble constituents from the adsorbents. Furthermore, the higher increase observed for the modified pumice may be attributed to the release of Na^+ ions loaded during the modification process. Turbidity increased from 0.2 to 1.3 NTU and 0.3 to 1.2 NTU for the natural and modified pumice samples respectively, namely close to the standard values and hence may not influence the disinfection process.

3.3. Effect of the contact time and the initial hardness agents concentration

The effects of the initial calcium and magnesium concentrations and the contact time on the removal efficiency of pumice are illustrated in Figure 5. As it can be seen, adsorption efficiency was improved by increasing the contact time and the initial ions concentration. While for natural pumice sample, the equilibrium time was not reached even after 240 minutes (Figs.5a and b), equilibrium was reached after 150 and 180 min for calcium and magnesium adsorption on the alkali-modified pumice (Figs.5c and d). Accordingly, for an initial metal concentration of 150 mg/L, 83% and 94% of calcium and 48% and 73% of magnesium were adsorbed by natural and modified pumices respectively, showing for both adsorbents a higher affinity for calcium over magnesium. Furthermore, alkali modification of pumice improved the adsorption capacity toward both tested cations.

Surface adsorption and ion exchange can be considered as the driving forces of ion removal. While bonding of metal ions to the surface can be considered as the main mechanism responsible for metal uptake by natural pumice, in addition to surface adsorption, ion exchange can also be involved in the case of the alkali-modified pumice leading to a

remarkable enhancement of the adsorption capacity [19]. Furthermore, alkali modification can contribute to the removal of impurities, which can unblock some pores improving accessibility to the active adsorption and ion exchange sites of the modified sample. Removal efficiency also showed an increase with the initial metal concentration, which can be attributed to an increase of the concentration gradient increasing the driving force [24].

Equilibrium data were analyzed by pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models. Fig.6 shows the fitting of equilibrium data onto pseudo-second order kinetic model and the related parameters are listed in Table 2. Pseudo-first order and intra-particle diffusion kinetic models showed lower correlation coefficient (R^2), and hence the corresponding data are not shown. Equilibrium data fitting confirmed that increasing the initial cations concentration increased sorption capacity of raw and modified adsorbents. As can be seen from Table 2, the experimental q_e values were close to those calculated. In addition and for both adsorbents, the rate constants (k_2) for calcium sorption were higher than those observed for magnesium, confirming the higher affinity of the studied adsorbents for calcium over magnesium.

3.4. Effect of the pH and the adsorbent mass

The pH of the solution should be considered as an important factor affecting metal adsorption process due to its impact on the degree of ionization of metal specie and the surface charge of the adsorbent. The effect of pH of the reaction mixture on the adsorption efficiency at various adsorbent doses was examined in order to optimize the adsorbent dosage and the pH. According to the results summarized in Fig.7, the highest adsorption capacity towards Ca^{+2} and Mg^{+2} ions was achieved at pH=6 for both natural and modified pumices and for all tested dosages. This optimal pH was in accordance with the zero point charge values (6.3 and 6.5 for natural and modified pumices respectively, see 2.7). As it is shown in Fig 7, at this pH 79 and 96% of calcium (Figs.7a and b) and 51 and 93% of magnesium

(Figs.7c and d) were removed by 10 g/L of the natural and modified pumice adsorbents, respectively. The lower removal efficiencies observed in acidic medium (i.e. pH in the range 2-5) can be attributed to the protonation of adsorbent functional groups or competition of H^+ with metal ions to bind and occupy the active sites of the adsorbents. On the other hand, in alkaline environment (i.e. pH in the range 8-10), the formation of metal hydroxide can be considered as the main reason for decreasing metal uptake [25]. Similar results were reported for the removal of magnesium by manganese oxide coated zeolite [26] and for the removal of calcium using raw sugar cane bagasse modified with tartaric acid and citric acid [27]. The highest removal capacity at pH=6, namely close to the zero point charges of natural and modified pumices, confirms that the studied pumice adsorbents can be considered as promising low cost adsorbents suitable for the removal of hardness ions from drinking water. The linear increase of the adsorption capacity for increasing adsorbent dosage indicated the accessibility of a larger number of sorption sites at higher dosage to adsorb calcium and magnesium ions. Contrarily, in the removal of calcium using raw and modified sugar cane bagasse, adsorption capacity remained constant above 100 mg adsorbent [27].

3.5. Effect of the temperature

The temperature effect in the range of 10°C to 60°C was studied and thermodynamic parameters were calculated and summarized in Table 3. As shown in Fig.8, while the effect of temperature on magnesium adsorption seemed to be negligible, a low maximum for the adsorption of calcium was observed at 20°C.

The Arrhenius equation was used to evaluate the nature of the adsorption (either physical (5–40 kJ/mol) or chemical (40–800 kJ/mol) :

$$\ln k_d = \ln A_o - E_a/RT \qquad (11)$$

Where A_o is the temperature independent factor called "frequency factor," E_a the activation energy (kJ/mol), R is the gas law constant (8.314 J/mol.K), and T is the absolute temperature

(*K*). A plot of *ln k* versus *1/T* yields to a straight line, from which the E_a and A_o can be obtained from the slope and the intercept, respectively. In the present work, the values of E_a and A_o were observed to be 175.32 kJ/mol and 144.45 kJ/mol for calcium and 135.82 kJ/mol and 122.53 kJ/mol for magnesium adsorption on the natural and modified pumice adsorbents respectively, indicating chemical adsorption rather than physisorption.

Thermodynamic parameters were determined for temperatures ranging from 20 to 60°C using the equilibrium constant k_d (q_e/C_e). The change in free energy (ΔG^o) was determined as follows (Eq. 12):

$$\Delta G^o = -RT \ln K_d \qquad (12)$$

Where, ΔG^o is the standard free energy (kJ/mol). The parameters of enthalpy ΔH^o (kJ/mol) and entropy ΔS^o (kJ/mol) related to the adsorption process were calculated from the following equation (Eq. 13):

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (13)$$

The parameters of enthalpy (ΔH^o) and entropy (ΔS^o) can be calculated from the slope and the intercept of the linear plot of ln k_d versus *1/T*. Fig.9 shows the thermodynamic plots and the related parameters are collected in Table 3. The values of ΔH^o were positive for all systems; showing that the sorption reaction was endothermic in nature. The negative ΔS^o value characterized a decrease in randomness at the solid/liquid interface during the sorption process. In addition, the values of standard free energy (ΔG^o) were positive indicating that the sorption of metals was not thermodynamically spontaneous.

3.6. Adsorption Isotherms

Langmuir, Freundlich and Temkin models were used to evaluate the results of adsorption tests. The different adsorption isotherms are illustrated in Fig.10 and the corresponding calculated data are collected in Table 4. The Fitting of equilibrium data onto

isotherm models shows that the Freundlich isotherm gave the highest regression coefficients for calcium and magnesium adsorption compared to Temkin and Langmuir isotherms. However, the closeness of the regression values indicated the relevance of the three isotherm models. The surface of the adsorbent contained most likely heterogeneous moieties which were uniformly distributed on the surface, accounting for Langmuir, Freundlich and Temkin isotherms [28]. The values of the separation factor (R_L) were calculated for various initial metal concentrations for raw and modified pumice adsorbents and were found between 0 and 1 (0.0176 to 0.0030 and 0.0292 to 0.0050 for calcium adsorption, 0.0400 to 0.0069 and 0.0320 to 0.0055 for magnesium adsorption on raw and modified pumice adsorbents, respectively), indicating a favorable adsorption process, as confirmed from the values of the Freundlich factor (n) which were in the range 1-10 (Table 4).

Maximum sorption capacities according to the Langmuir constant (q_{max}) for calcium and magnesium adsorption using various natural adsorbents are listed in Table 5 to allow comparison with the results from the present work. Maximum sorption capacities by raw and modified pumices were 62.34 and 57.27 mg/g for calcium and 44.53 and 56.11 mg/g for magnesium respectively, namely higher than those reported in Table 5, except for the adsorption of magnesium on pecan nutshell.

3.7. Binary System

In order to study the interfering effect of Ca^{+2} and Mg^{+2} ions one another, adsorption tests were conducted in the optimal conditions using a mixture of Ca^{+2} and Mg^{+2} cations (100 mg/L each) (Fig.11). Cation uptake was 63% and 74% for calcium and 27% and 59% for magnesium on the natural and modified pumices, respectively. It can be noticed that equilibrium time and adsorption efficiency were lower compared to the values observed in single ion adsorption tests, which can be attributed to a competition between the two cations for occupying the active sites leading to a faster saturation of the adsorbent in the

simultaneous presence of calcium and magnesium. Nevertheless and similarly to the single ion adsorption tests, calcium showed higher adsorption compared to magnesium indicating a higher selectivity of the adsorbents for calcium. These results also showed the efficiency of natural and modified pumices for the removal of calcium and magnesium from water streams.

3.8. Effect of other co-existing anions

Actual water samples contain a wide range of anionic species that may influence on the adsorption of calcium and magnesium ions. In order to study the performance of the pumice adsorbents in actual situation, a synthetic water sample containing chloride (450 mg/L), nitrate (25 mg/L) and sulfate (325 mg/L), as well as 100 mg/L of calcium and 100 mg/L of magnesium, was prepared. This sample simulated the actual water of the Karaj Water Supply system. The total dissolved solid (TDS) of the water sample was 1150 mg/L and the conductivity was adjusted by sodium chloride to 1850 μs/cm (according to the Karaj water supply system). The adsorption tests were conducted using 6 g/L of either natural or modified pumice adsorbents at pH 6 for 240 minute at room temperature. According to the results, counter ions (i.e. anions) decreased the adsorption capacity of the adsorbents for Ca^{2+} and Mg^{2+} cations, since removal efficiencies decreased to 53% and 61% for calcium and to 24% and 51% for magnesium for the natural and modified adsorbents, respectively. From this, the total remaining hardness in the treated water sample by using the natural and modified pumice adsorbents should be 429 and 297.5 mg/L as $CaCO_3$ respectively, namely close to the advocated value, since the total hardness for drinking water should be less than 300 mg/L as $CaCO_3$ (AWWA, 2005); hence the alkali modified pumice can be considered as a promising adsorbent for water softening. In addition, nitrate, chloride and sulfate concentrations were also measured after treatment. Removal efficiencies were 5.6 and 33% for nitrate, 33 and 63% for chloride and 51 and 59% for sulfate for natural and modified pumices, respectively.

Furthermore, the conductivity of the water sample treated with the natural and modified adsorbents increased to 1975 and 1936 μs/cm, respectively. This should be related to the increase of the total dissolved solid, which were 1234 and 1221 mg/L after water treatment with the natural and modified pumices respectively, most likely due to partial dissolution of the adsorbents. Overall, although the co-existing ions can interfere in the sorption of calcium and magnesium, final total hardness can meet the required standard level when the alkali modified pumice was used as an adsorbent.

3.9. Regeneration of the saturated adsorbents

Regeneration experiments were conducted to study the reusability of the spent adsorbents, which is a very important parameter in terms of economical feasibility of the developed process. Regeneration using sodium hydroxide solution was carried out on the spent natural and modified pumice samples. Regeneration percentage of the spent adsorbent versus reaction time is illustrated in Fig.12. Maximum recovery of the adsorbed calcium and magnesium was achieved in less than 300 minutes leading to 99 and 92% desorption of the adsorbed calcium and 100 and 89% of the adsorbed magnesium from the natural and modified pumices, respectively. Furthermore, maximum cation desorption for saturated natural pumice was observed after 510 min of regeneration, while only 300 min of regeneration was needed to achieve maximum cation desorption of the saturated modified pumice adsorbent. It should be noticed that even if the modified pumice stone showed higher sorption capacity for magnesium rather than natural pumice, its regeneration potential was lower than that of the natural pumice.

4. Conclusion

Softening of hard water by removing Ca^{2+} and Mg^{2+} cations was studied using natural and alkali-modified pumices as adsorbents. Increasing the mass of adsorbent, the contact time or the initial ions concentration led to an increase of cations removal. The

studied pumice adsorbents showed a higher selectivity for calcium adsorption if compared to magnesium. For both adsorbents, an increase of EC and turbidity was shown, which can be attributed to a partial dissolution of the adsorbent; this increase remained however limited. After treating synthetic water solution simulating an actual water stream with the alkali modified pumice, total hardness of the treated sample met the required standard for drinking water.

Acknowledgment

This work was supported by Alborz University of Medical Sciences. The authors are grateful to Alborz University of Medical Sciences for financial support of this work.

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Figure Captions

Fig.1. XRD patterns of natural pumice (a) and alkali modified pumice (b)

Fig.2. SEM images of natural pumice (a) and alkali modified pumice (b)

Fig.3. FTIR spectra of natural pumice (a) and alkali modified pumice (b)

Fig.4. Effect of natural and modified pumices on conductivity and turbidity (6 g/L adsorbent, pH 6.5, room temperature, agitation speed 200 rpm, 5 μs/cm initial EC and approximately zero initial turbidity)

Fig.5. Effect of initial cation concentrations and contact time on the removal efficiency, (a) Ca^{2+} on natural pumice, (b) Ca^{2+} on modified pumice, (c) Mg^{2+} on natural pumice, (d) Mg^{2+} on modified pumice (experimental conditions: pH=6.5, adsorbent dose 6 g/L, room temperature, 200 rpm agitation speed).

Fig.6. Fitting of equilibrium data onto pseudo-second order kinetic model, (a) Ca^{2+} on natural pumice, (b) Ca^{2+} on modified pumice, (c) Mg^{2+} on natural pumice, (d) Mg^{2+} on modified pumice

Fig.7. Effect of pH and adsorbent dosage on calcium and magnesium removals, (a) Ca^{2+} on natural pumice, (b) Ca^{2+} on modified pumice, (c) Mg^{2+} on natural pumice, (d) Mg^{2+} on

modified pumice (contact time 210 min, ions concentration 100 mg/L, room temperature, 200 rpm agitation).

Fig.8. Effect of the temperature on the removal efficiency (ions concentration 100 mg/L, adsorbent 6 g/L, pH 6.5, contact time 210 min)

Fig.9. Thermodynamic illustration for calcium and magnesium adsorption on natural and modified pumices

Fig.10. Fitting of equilibrium data onto isotherm models, (a) Freundlich, (b) Langmuir, (c) Temkin

Fig.11. Sorption of calcium and magnesium in binary system (adsorbent 6 g/L, pH 6.5, ions concentration 100 mg/L, room temperature, 200 rpm agitation speed)

Fig.12. Regeneration of the saturated adsorbents (spent adsorbent: 6 g/L, initial calcium and magnesium concentration: 100 mg/L each and 2 N NaOH used for regeneration).

Table 1 Chemical compaction of raw used adsorbent (w/w)

Component	%	Component	%
SiO_2	63.45	SrO	0.09
Al_2O_3	17.24	MgO	1.03
TiO_2	0.37	K_2O	2.16
P_2O_5	0.21	SO_3	0.16
CaO	3.22	Na_2O	2.00
Fe_2O_3	2.86	Cl^-	0.30

Table 2 Pseudo second order kinetic parameters for the present work

	Calcium on raw adsorbent				Calcium on modified adsorbent			
	k_2	$q_{e,\,calc}$	$q_{e,\,exp}$	R^2	k_2	$q_{e,\,calc}$	$q_{e,\,exp}$	R^2
50 mg/L	0.63	5.59	5.25	0.98	0.71	6.30	5.91	0.97
100 mg/L	0.67	8.99	8.83	0.99	0.82	17.82	15.33	0.98
150 mg/L	0.73	16.05	15.75	0.98	0.89	25.70	23.50	0.99
	Magnesium on raw adsorbent				Magnesium on modified adsorbent			
	k_2	$q_{e,\,calc}$	$q_{e,\,exp}$	R^2	k_2	$q_{e,\,calc}$	$q_{e,\,exp}$	R^2
50 mg/L	0.57	2.61	2.33	0.99	0.60	5.77	4.25	0.97
100 mg/L	0.59	3.61	3.16	0.98	0.61	13.26	10.83	0.98
150 mg/L	0.61	14.49	12.33	0.97	0.65	21.83	18.25	0.97

Table 3 Parameters collected from the thermodynamic model

	ΔH^0	ΔS^0	ΔG^0					
T (K)			283	293	303	313	323	333
Raw-Ca^{+2}	0.493	-10.13	3063	3068	3596	3929	4054	4292
Modified-Ca^{+2}	0.257	-6.41	1993	1816	2258	2332	2536	2614
Raw-Mg^{+2}	0.418	-22.51	6555	6787	7148	7521	8056	8305
Modified-Mg^{+2}	0.088	-11.73	3359	3478	3596	3822	3944	*4066*

Table 4 Parameters collected from isotherm models

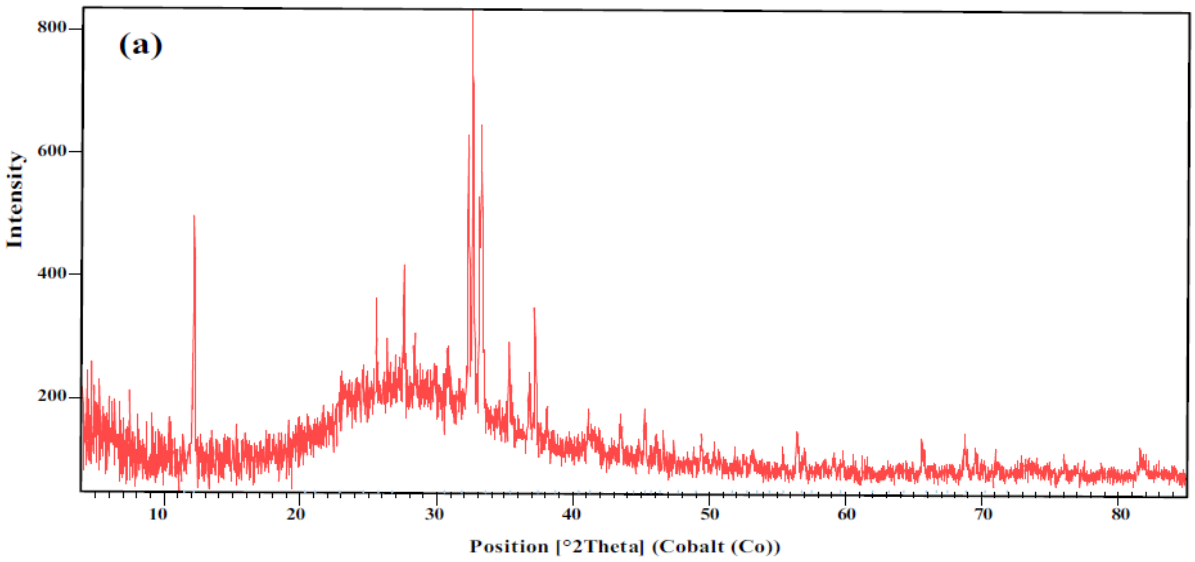
Isotherm Model	parameter	Raw-Ca^{+2}	Modified- Ca^{+2}	Raw- Mg^{+2}	Modified-Mg^{+2}
Freundlich	r^2	0.991	0.996	0.989	0.989
	K_f	7.23	9.24	7.9	7.35
	n	0.263	0.357	0.384	0.294
	r^2	0.960	0.911	0.965	0.949
Langmuir	q_m	62.34	57.27	44.53	56.11
	b	2.23	1.33	0.96	1.21
	r^2	0.905	0.937	0.906	0.911
Temkin	b_1	68.31	82.44	109.03	79.02
	k_t	0.8	1.69	0.53	*0.66*

Table 5 Maximum sorption capacity of some adsorbents for calcium and magnesium

Adsorbent	$q_{max\ (mg/g)}$		Reference
	Ca^{+2}	Mg^{+2}	
Black carrot residues	-------	3.871	[25]
Activated Chilean zeolites	------	0.774	[26]
Natural zeolite	-------	0.259	[26]
Manganese oxide coated zeolite	-------	1.123	[26]
Sugar cane bagasse modified with citric acid	26.52	-------	[27]
Sugar cane bagasse modified with tartaric acid	14.72	-----	[27]
Green tomato husk	------	6.76	[29]
Chemically modified cellulose	15.6	13.5	[30]
Sugar cane bagasse	46.1	23.50	[30]
Rice husk	-------	3.87	[31]
Pecan nutshell	------	103.8	[32]
Kaolinite	-------	0.446	[33]
Raw pumice	57.27	44.53	Present work

Modified pumice	62.34	56.11	Present work

Figure 1



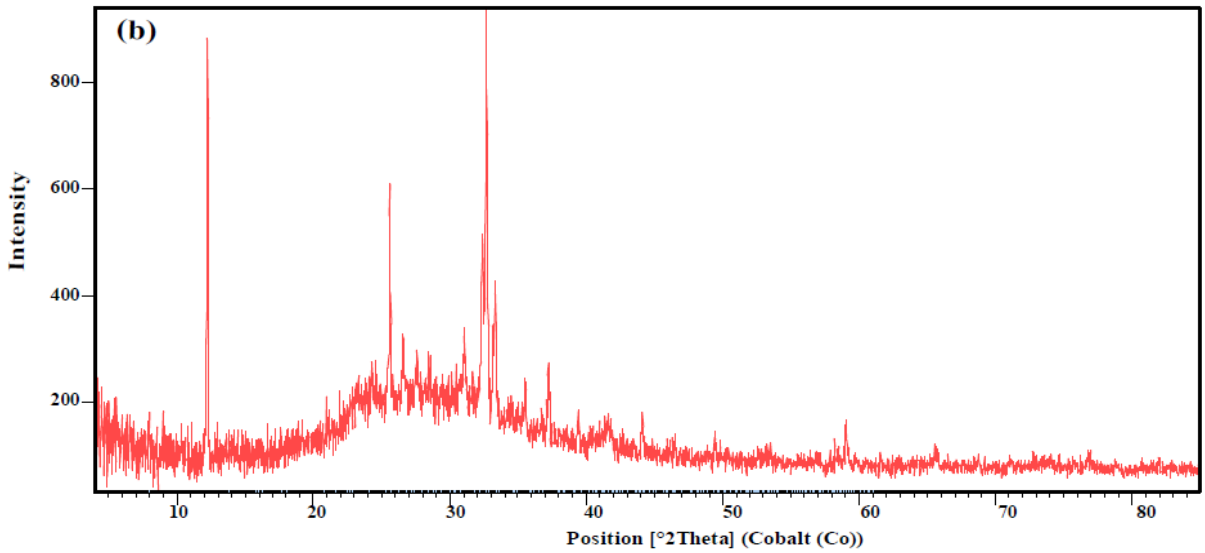
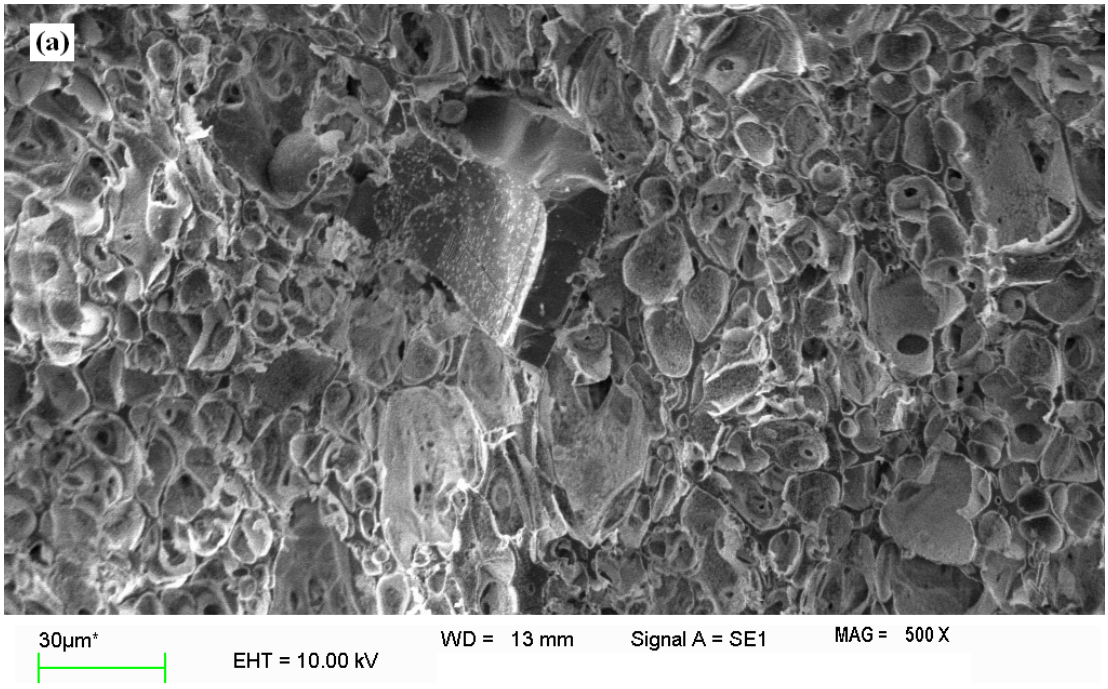

(b)
Intensity
800
600
400
200
10
20
30
40
50
60
70
80
Position [°2Theta] (Cobalt (Co))

Figure 2


(a)
30µm*
EHT = 10.00 kV
WD = 13 mm
Signal A = SE1
MAG = 500 X

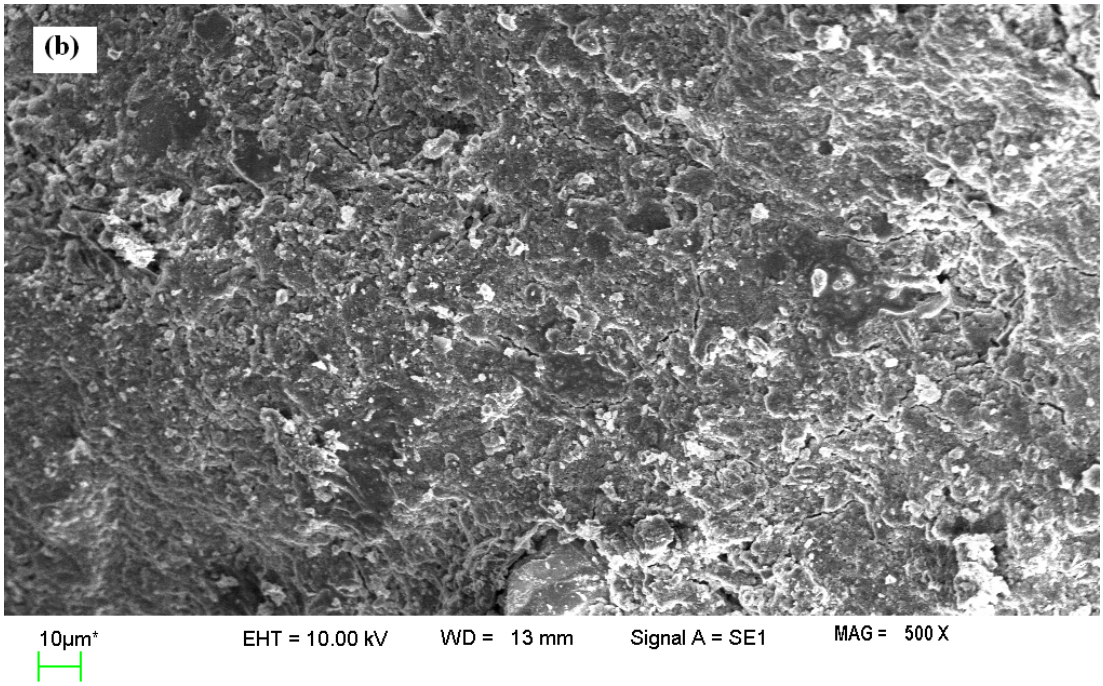
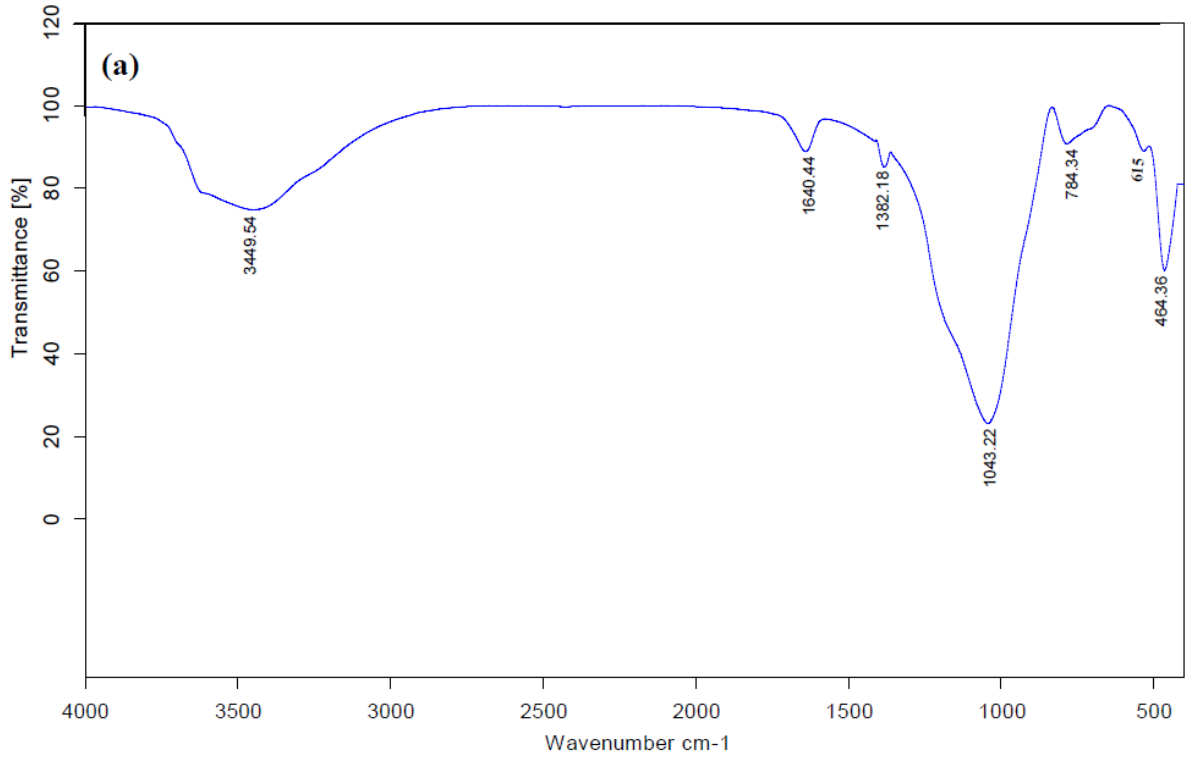


Figure 3


(a)
Transmittance [%]
0
20
40
60
80
100
120
3449.54
1640.44
1382.18
1043.22
784.34
615
464.36
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

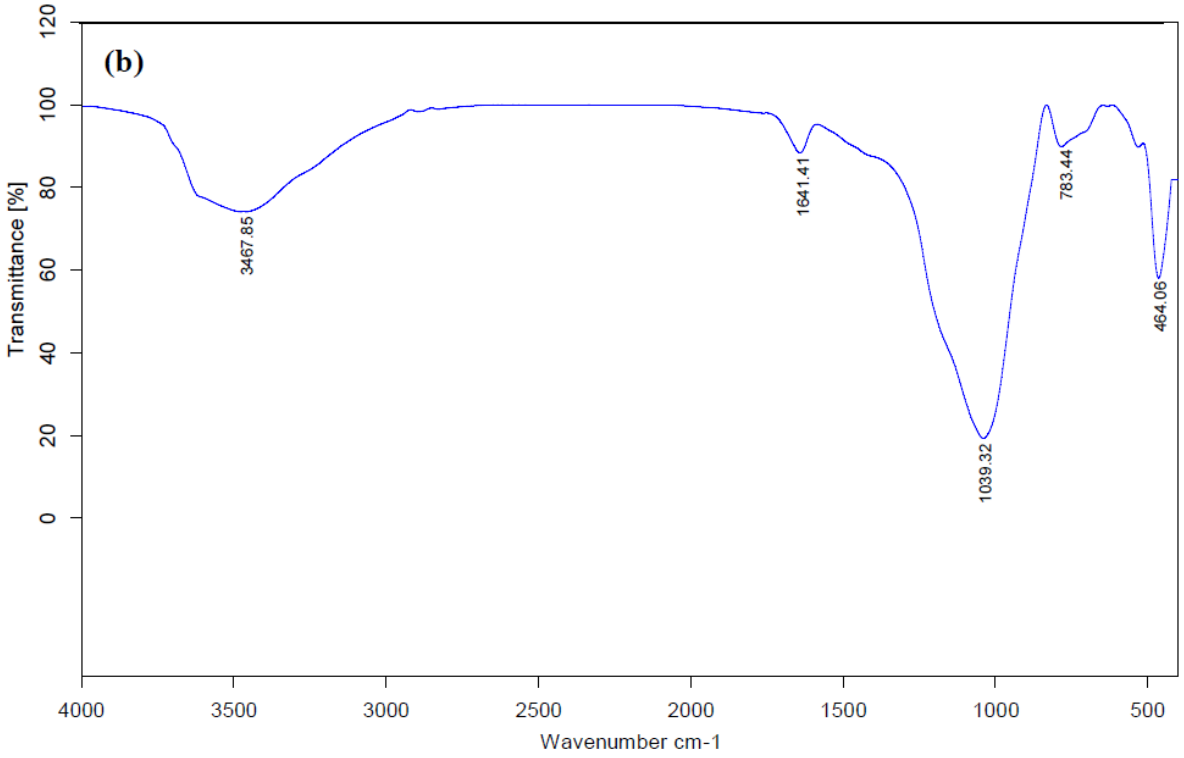

(b)
Transmittance [%]
0
20
40
60
80
100
120
3467.85
1641.41
1039.32
783.44
464.06
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Figure 4

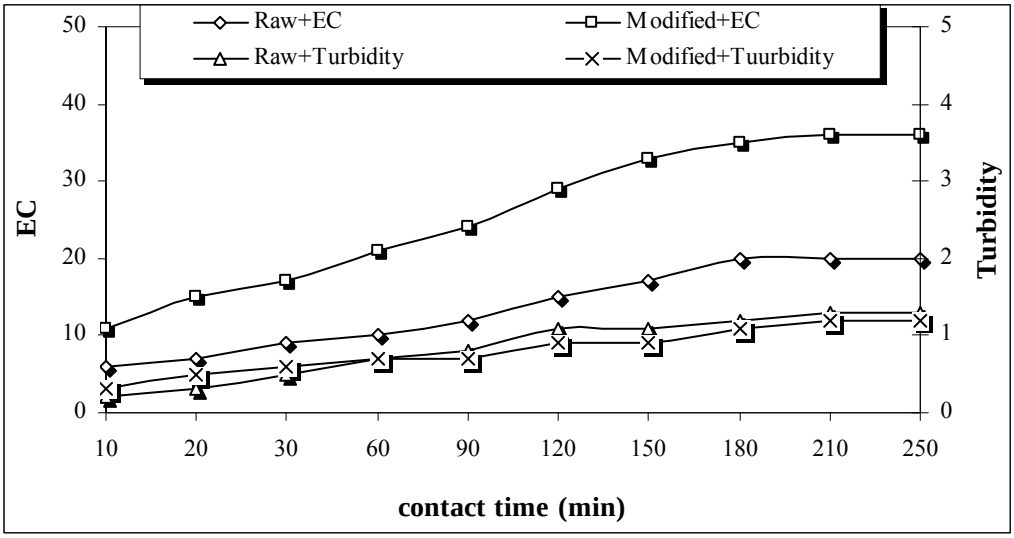
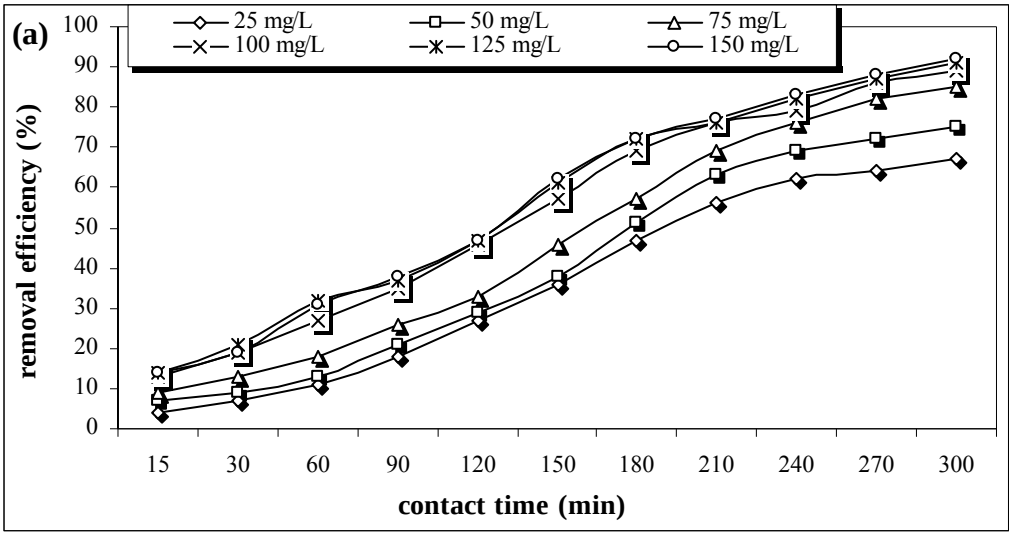
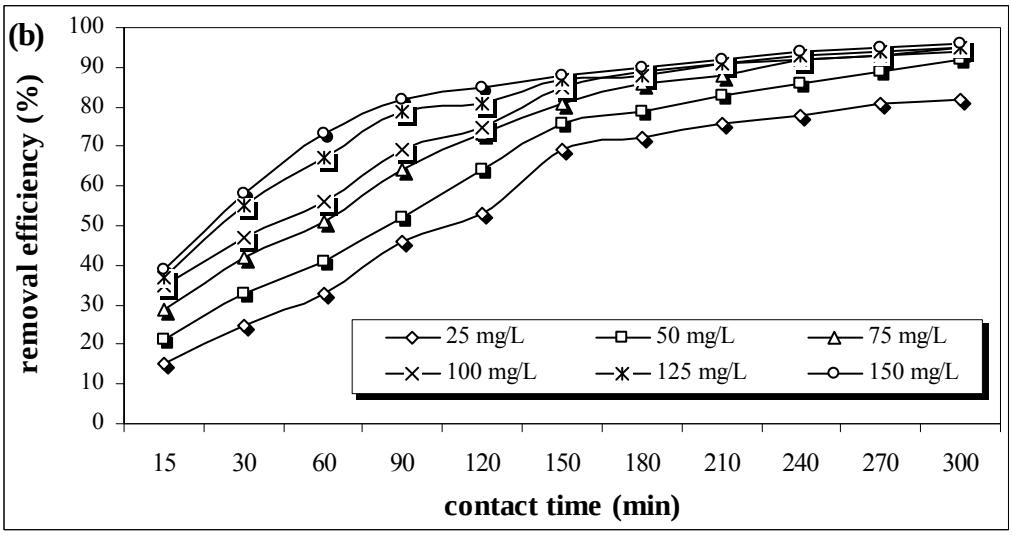
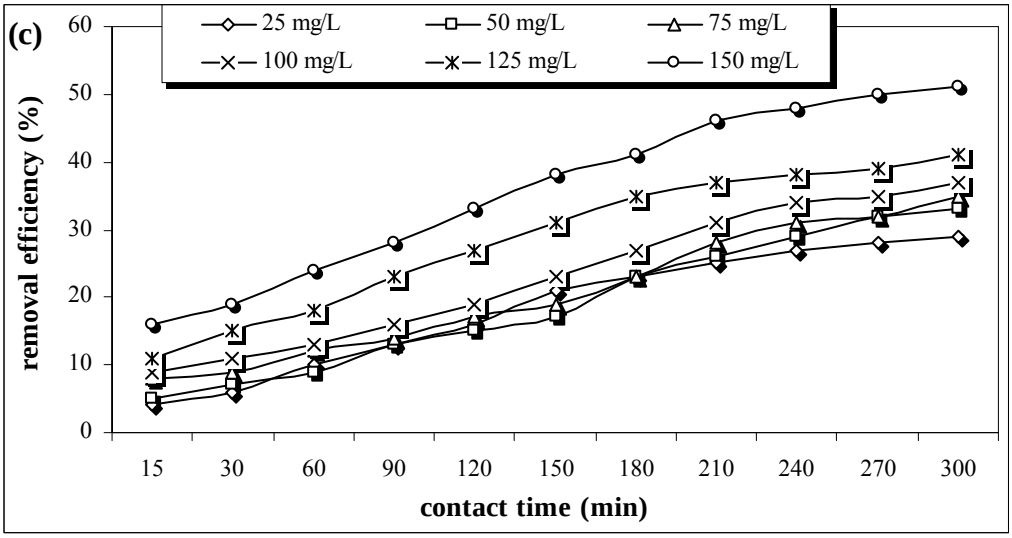

Raw+EC
Modified+EC
Raw+Turbidity
Modified+Tuurbidity
EC
Turbidity
contact time (min)
0
10
20
30
40
50
0
1
2
3
4
5
10
20
30
60
90
120
150
180
210
250

Figure 5


(a)
25 mg/L
50 mg/L
75 mg/L
100 mg/L
125 mg/L
150 mg/L
removal efficiency (%)
contact time (min)


(b)
25 mg/L
50 mg/L
75 mg/L
100 mg/L
125 mg/L
150 mg/L
removal efficiency (%)
contact time (min)


(c)
25 mg/L
50 mg/L
75 mg/L
100 mg/L
125 mg/L
150 mg/L
removal efficiency (%)
contact time (min)

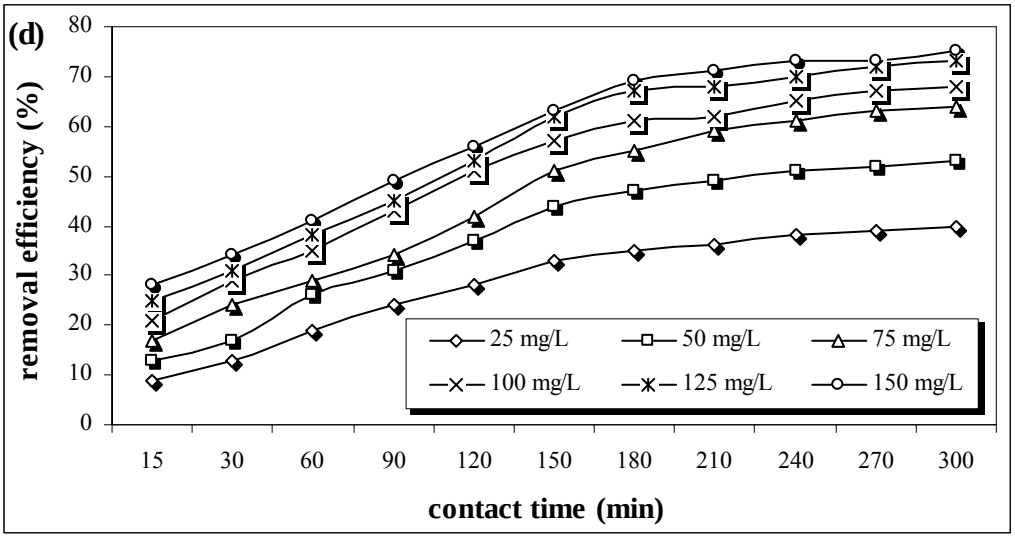
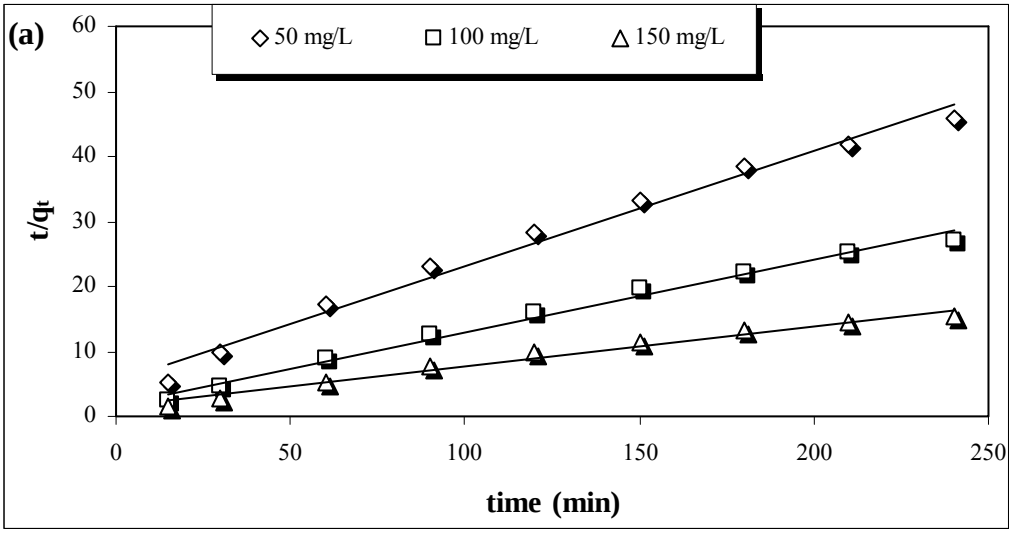
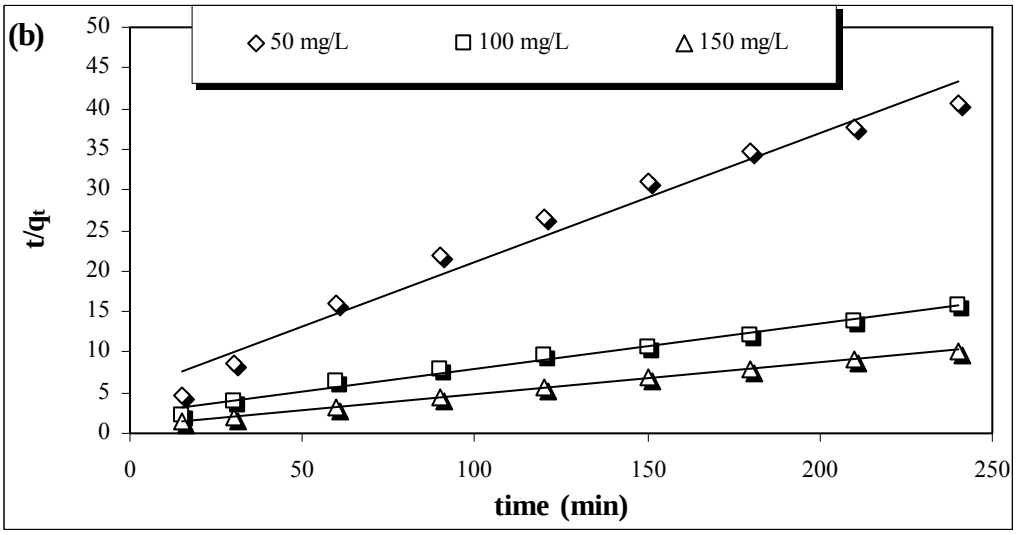
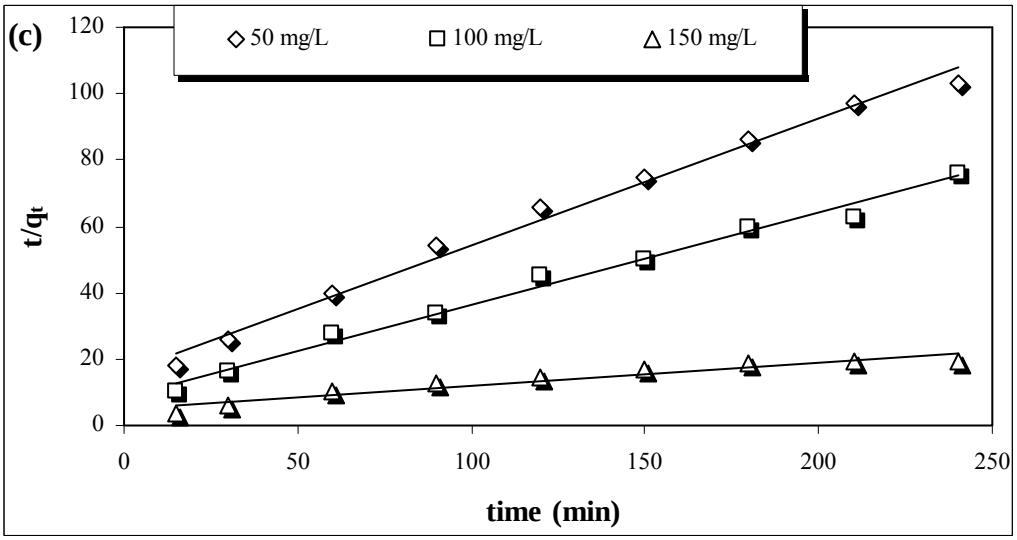

(d)
removal efficiency (%)
80
70
60
50
40
30
20
10
0
15
30
60
90
120
150
180
210
240
270
300
contact time (min)
25 mg/L
50 mg/L
75 mg/L
100 mg/L
125 mg/L
150 mg/L

Figure 6


(a)
◇ 50 mg/L
□ 100 mg/L
△ 150 mg/L
t/qt
time (min)


(b)
◇ 50 mg/L
□ 100 mg/L
△ 150 mg/L
t/qt
time (min)


(c)
◇ 50 mg/L
□ 100 mg/L
△ 150 mg/L
t/qt
time (min)

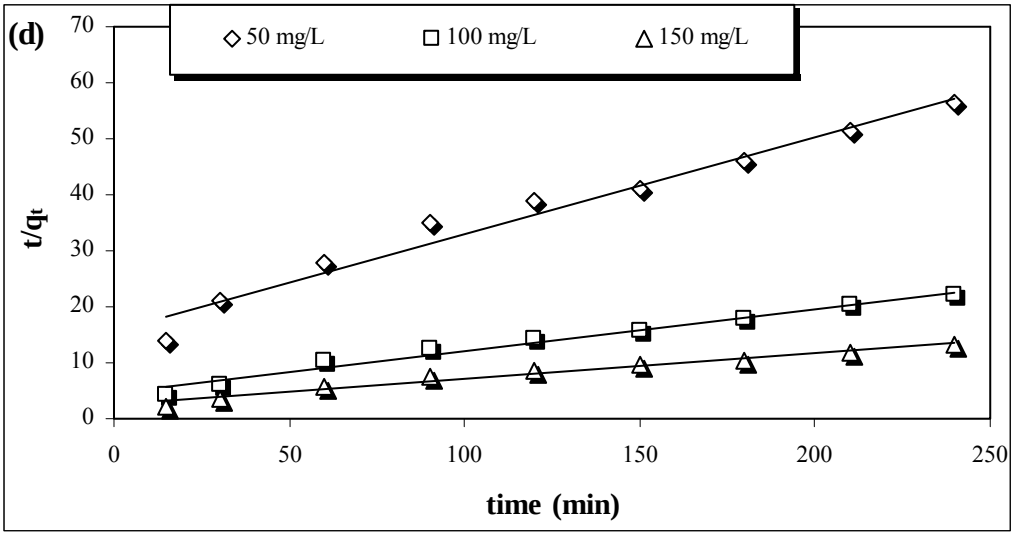
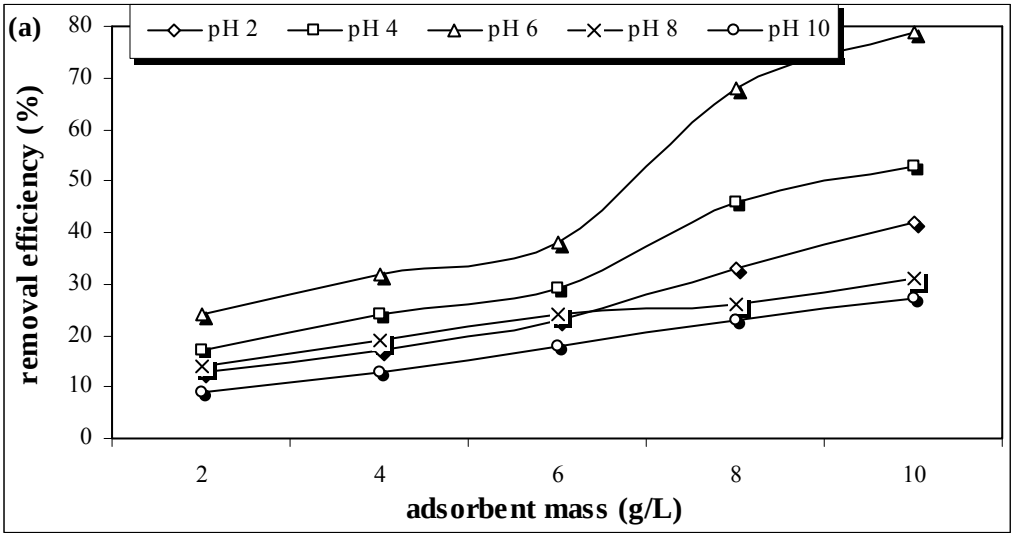
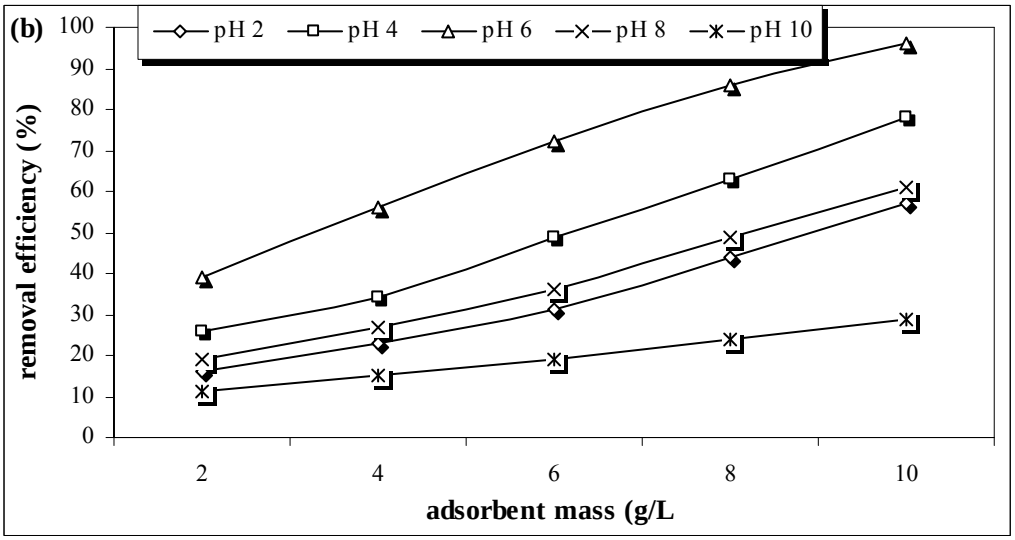

(d)
50 mg/L
100 mg/L
150 mg/L
t/qt
time (min)
0
10
20
30
40
50
60
70
0
50
100
150
200
250

Figure 7


(a)
pH 2
pH 4
pH 6
pH 8
pH 10
removal efficiency (%)
0
10
20
30
40
50
60
70
80
2
4
6
8
10
adsorbent mass (g/L)


(b)
pH 2
pH 4
pH 6
pH 8
pH 10
removal efficiency (%)
0
10
20
30
40
50
60
70
80
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4
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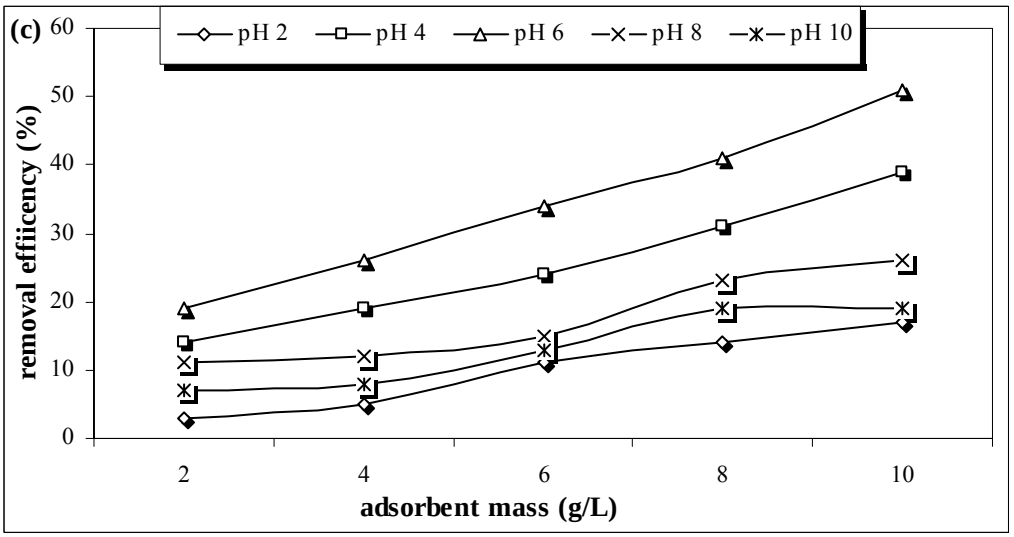
8
10
adsorbent mass (g/L


(c)
pH 2
pH 4
pH 6
pH 8
pH 10
removal effiicency (%)
0
10
20
30
40
50
60
2
4
6
8
10
adsorbent mass (g/L)

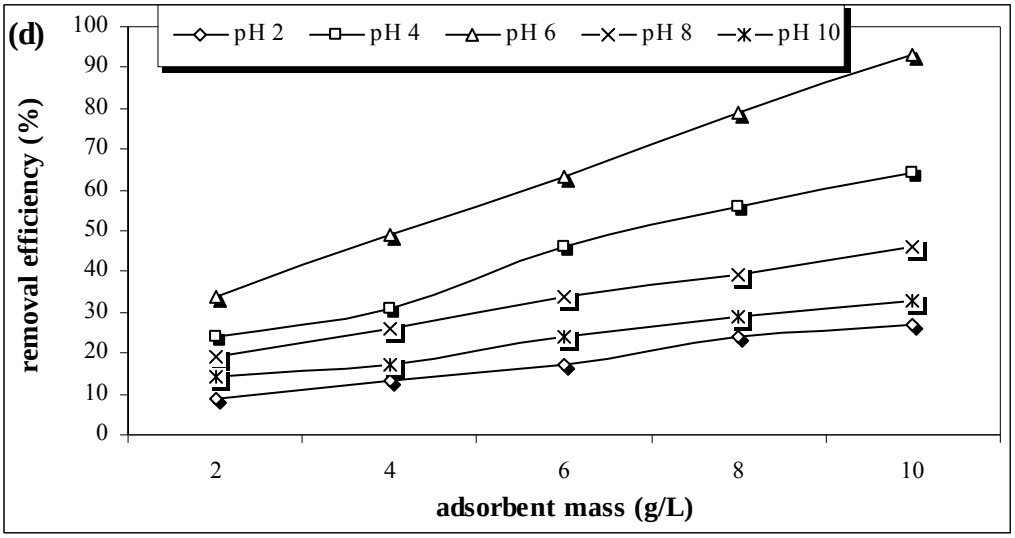

(d)
pH 2
pH 4
pH 6
pH 8
pH 10
removal efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
adsorbent mass (g/L)

Figure 8

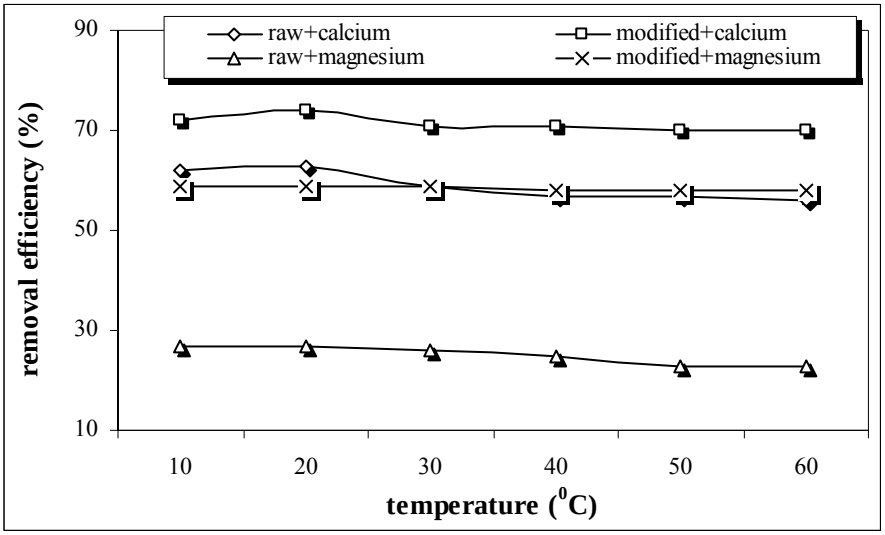

raw+calcium
modified+calcium
raw+magnesium
modified+magnesium
removal efficiency (%)
90
70
50
30
10
10
20
30
40
50
60
temperature (0C)

Figure 9

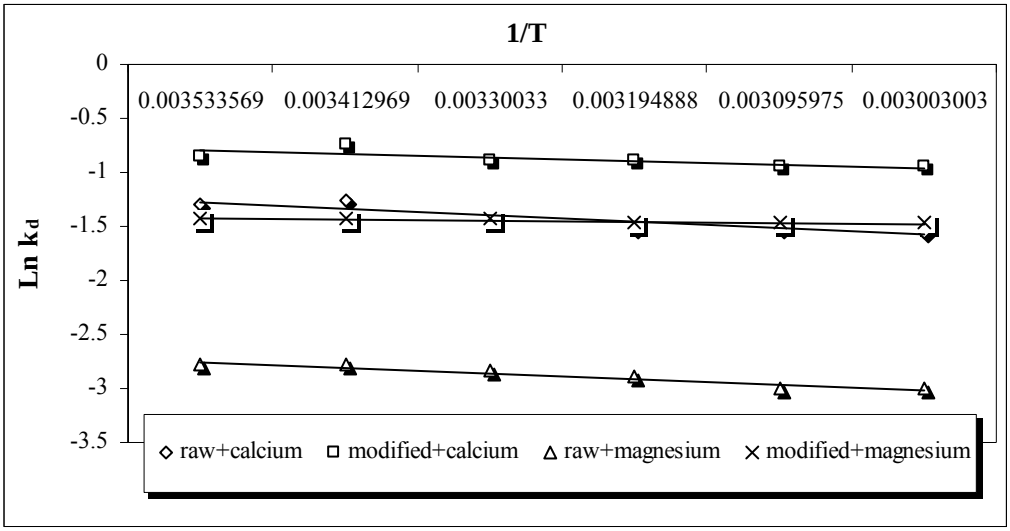
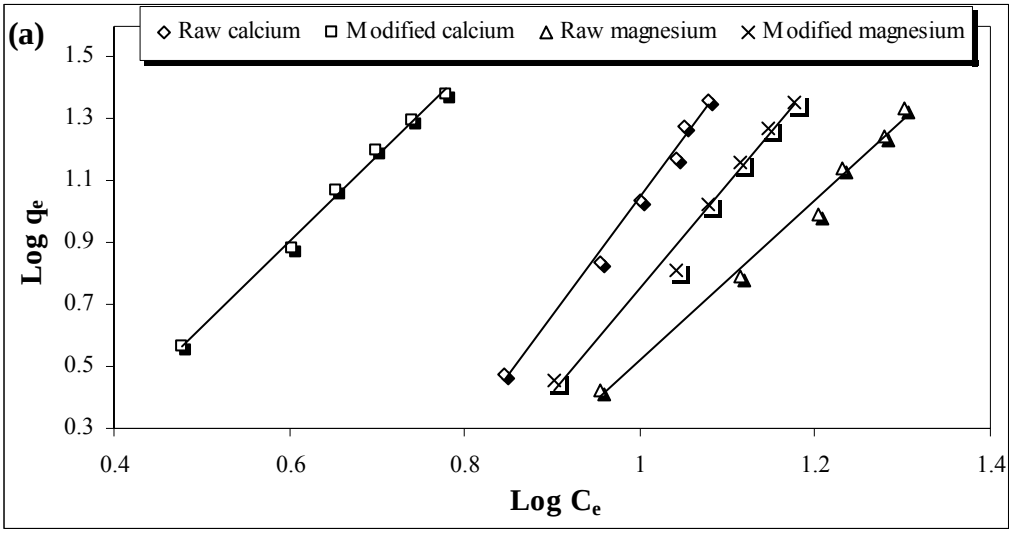
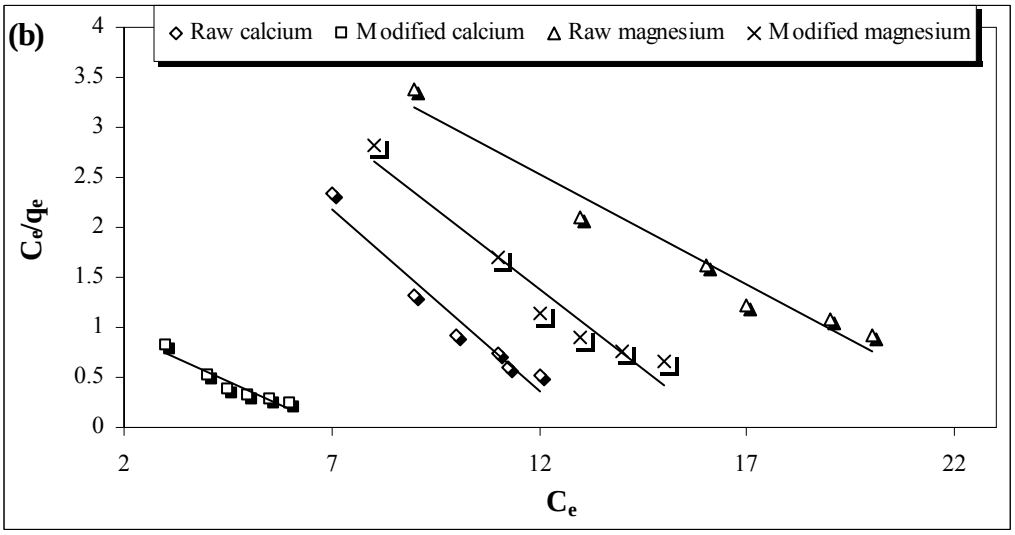

1/T
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
0.003533569
0.003412969
0.00330033
0.003194888
0.003095975
0.003003003
Ln kd
raw+calcium
modified+calcium
raw+magnesium
modified+magnesium

Figure 10


(a)
Raw calcium
Modified calcium
Raw magnesium
Modified magnesium
Log qe
Log Ce
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.4
0.6
0.8
1
1.2
1.4


(b)
Raw calcium
Modified calcium
Raw magnesium
Modified magnesium
Ce/qe
Ce
4
3.5
3
2.5
2
1.5
1
0.5
0
2
7
12
17
22

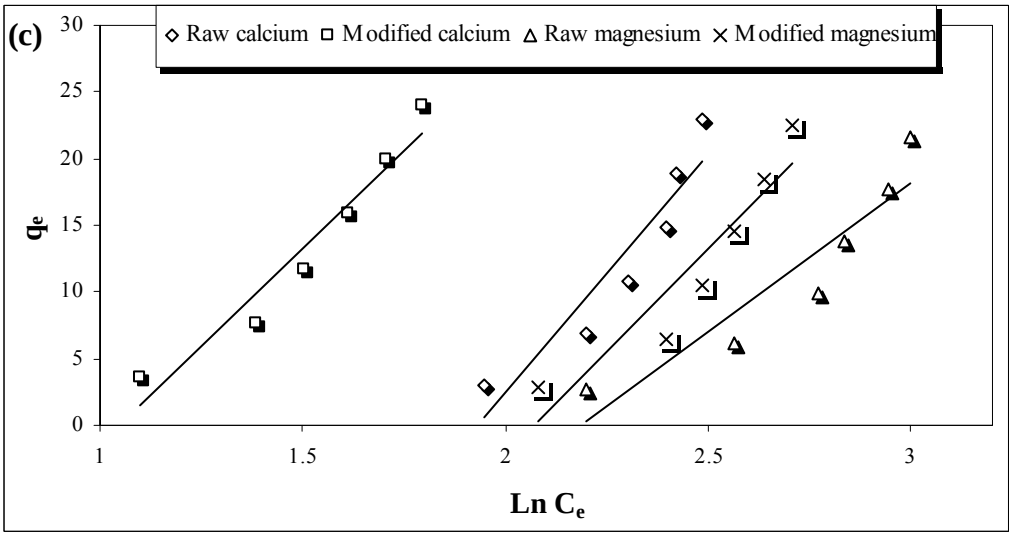

(c)
Raw calcium
Modified calcium
Raw magnesium
Modified magnesium
qe
Ln Ce
30
25
20
15
10
5
0
1
1.5
2
2.5
3

Figure 11

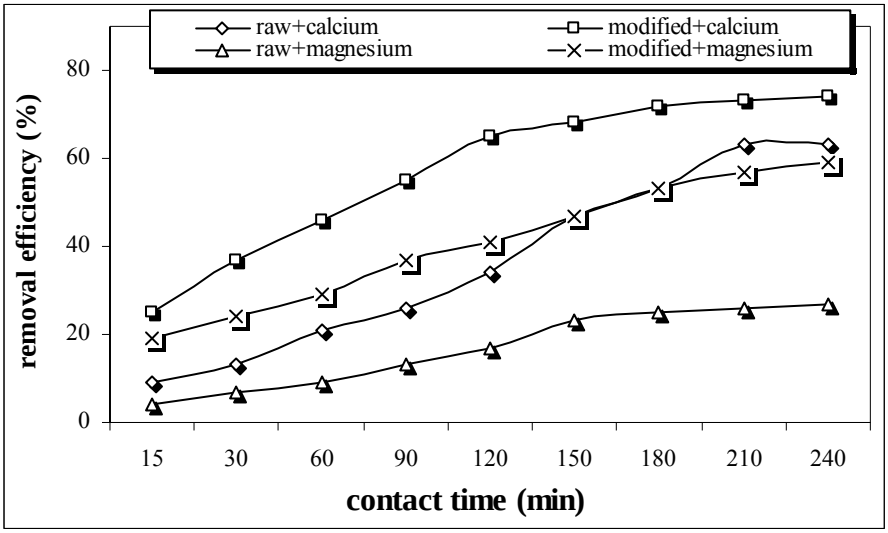
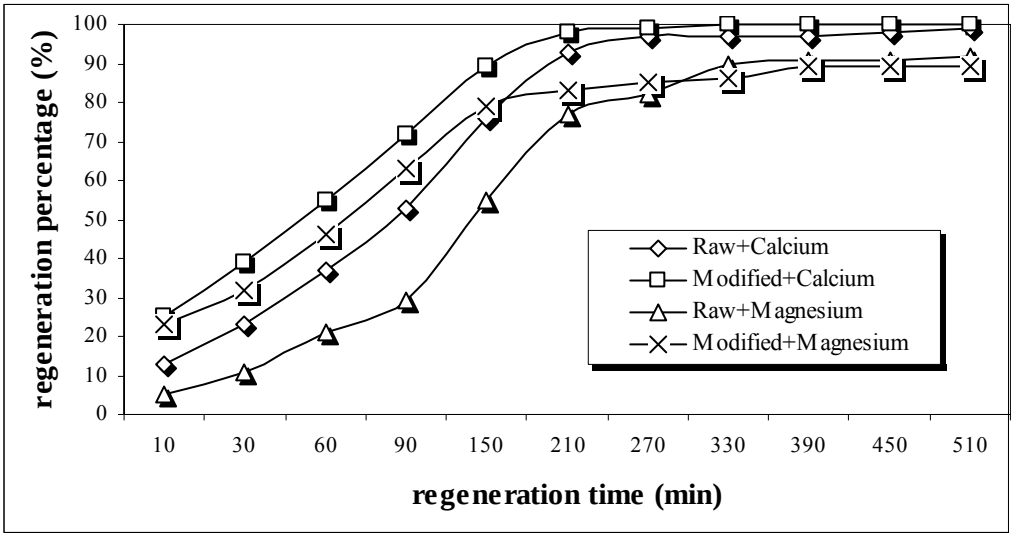

raw+calcium
modified+calcium
raw+magnesium
modified+magnesium
removal efficiency (%)
0
20
40
60
80
15
30
60
90
120
150
180
210
240
contact time (min)

Figure 12


regeneration percentage (%)
100
90
80
70
60
50
40
30
20
10
0
10
30
60
90
150
210
270
330
390
450
510
regeneration time (min)
Raw+Calcium
Modified+Calcium
Raw+Magnesium
Modified+Magnesium